

Chapter 2 Measurement of the Heat of Combustion Using a Bomb Calorimeter

1. Objective:

- Measure the heat of combustion of liquid and solid fuels (Charcoal, kerosene, etc.) per unit mass or per unit mole, in oxygen using the Bomb Calorimeter.
- Understand the differences in the heat of combustion between different fuels (including oxygenated fuels such as alcohol).
- Understand the effect of incomplete combustion on the heat of combustion.

2. Introduction

2.1 Definition

Heat of combustion is a very important parameter in choosing fuels for vehicles from transportation to rocket propulsion. A higher heat of combustion usually implies higher engine efficiency and propulsion performance.

Heat of combustion depends on the thermodynamic process and the final combustion products. There are *two different ways* to define the heat of combustion depending on whether the combustion process occurs at constant volume (e.g. gasoline engine) or at constant pressure (e.g. gas turbine engine). For **constant volume combustion**, if the initial temperature is the **same** as the final temperature, the change of internal energy will be converted to thermal energy: *the heat of combustion at constant volume*

$$\Delta Q = Q_R - Q_P = U_P - U_R = \Delta U_{P-R} . \quad 1$$

Here Q is the total heat and U the total internal energy, and R and P indicate the initial reactants and the final products respectively. Similarly, for **constant pressure combustion** with the **same** initial and final temperatures, the change of enthalpy will be converted to thermal energy: *the heat of combustion at constant pressure*

$$\Delta Q = Q_R - Q_P = H_P - H_R = \Delta H_{P-R} . \quad 2$$

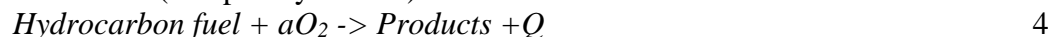
Here H is the total enthalpy, $H=U + pV$, P is the pressure, and V is the total volume. Therefore, from above definition, the difference in the heat of combustion between the constant pressure and the constant volume combustion is

$$\Delta H_{P-R} - \Delta U_{P-R} = p(V_P - V_R) = (n_P - n_R)RT . \quad 3$$

Here n is the total mole number, T is the gas temperature, and R is the gas constant.

2.2 Heat of combustion of hydrocarbon fuels

Let us consider the constant volume combustion of one mole of hydrocarbon fuel in oxygen. The ideal chemical reaction (completely burned) can be written as



where a is the **stoichiometric coefficient**, which means one mole fuel needs a mole oxygen to burn completely.

If we can measure the combustion heat release Q , the **heat of combustion** (q) can be simply calculated by

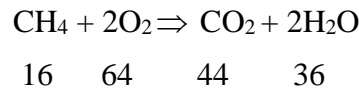
$$q=Q/m \quad 5$$

where m is the mass of fuel. Therefore, the question becomes how to ensure the complete combustion and how to measure the combustion heat release Q .

To ensure a **complete combustion** of fuel, the amount oxygen **must be larger** than the oxygen required for complete oxidization of fuel. For example, for methane (CH_4) combustion in oxygen, the combustion reaction in Eq. 4 becomes



Therefore, one mole CH_4 needs two moles of oxygen to completely consume CH_4 and form CO_2 and H_2O . The mass conservation is rewritten as



Therefore, the **stoichiometric fuel/oxygen ratio** is

$$\left(\frac{F}{A}\right)_s = \frac{\text{mass of fuel for complete consumption of fuel and O}_2}{\text{mass of air for complete consumption of fuel and O}_2} = \frac{16}{64}. \quad 7$$

In **fuel lean** and **fuel rich** cases, the **fuel/air ratio (FAR)** are respectively less and larger than the stoichiometric FAR. As such, it is convenient to use the ratio of actual FAR to the stoichiometric FAR to determine whether the mixture is fuel rich or fuel lean. This ratio is termed the mixture **equivalence ratio**, ϕ , and is defined as

$$\phi = \frac{FAR}{FAR|_{stoich}} = \frac{\text{actual fuel/air ratio}}{\text{fuel/air}|_s}, \quad \begin{array}{l} \phi > 1, \text{ Fuel rich} \\ \phi = 1, \text{ Stoichiometric} \\ \phi < 1, \text{ Fuel lean} \end{array} \quad 8$$

Therefore, ϕ larger, equal, and less than unity denotes fuel rich, stoichiometric, and fuel lean conditions, respectively,. Thus, from the above discussions and Eq.4, to completely consume the fuel in a combustion process, the oxygen mass (see Eq. 4) must be

$$m_{\text{O}_2} (\text{Mass of oxygen}) = \frac{pV}{RT} \geq 32a * m_F. \quad 9$$

In fact, in the experiment, you know the mass of fuel (m_F) and chamber volume V . The amount of oxygen is determined by the oxygen pressure in Eq.9.

To measure the heat release Q for constant volume combustion, Eq.1 tells you that you need a system that has a very large heat capacity to absorb the combustion heat release and to keep the final temperature very close to the initial temperature.

Figure 1 is the schematic of the experimental model to measure the combustion heat release Q . The metal Bomb Calorimeter (Fig.1) has a volume of 342 mL and is immersed in an insulated water bath. First, fuel (less than 1 gram) is loaded in the fuel vessel and a fuse wire is put on the electrodes (**keep the wire close to the fuel surface to ensure successful ignition**). Second, the bomb calorimeter is closed and filled with oxygen (**less than 20 atm**). Third, the fuel/oxygen mixture will be ignited electrically using a fuse-wire (make sure you record the water temperature before you ignite it). After the constant volume combustion, the heat generated from the combustion of the fuel sample and the ignition wire is transferred to the surrounding water

and raises the water temperature. The water temperature increase produced by this heat transfer will be measured using a thermocouple and recorded as a function of time by the LabView program “**Bomb Calorimeter.vi**”. Therefore, to calculate the combustion heat release, the effective heat capacity of the bomb calorimeter system (including water, gas mixture, and calorimeter etc.) has to be calibrated or standardized.

2.3 Calibration of the bomb calorimeter

The calibration involves the operation of the calorimeter on a standard fuel sample (e. g. benzoic acid) from which the energy equivalent or effective heat capacity can be determined. The **effective heat capacity** (W) of the bomb calorimeter is the heat required to raise its temperature by one degree, expressed in cal/K.

Example of calibration: By assuming a complete combustion and that the change of the heat capacity of the gas mixture before and after combustion is negligible compared with total heat capacity of water and calorimeter, the effective heat capacity can be obtained by the ratio of total heat release to the change of the temperature before and after the combustion

$$C = \frac{qm_F + l_{\text{wire}}q_{\text{wire}}}{\Delta T}, \text{ where} \quad 10$$

C : energy equivalent of the bomb calorimeter (cal/K),

q : heat of combustion of the standard fuel sample per unit mass at constant volume combustion in oxygen (e. g. **benzoic acid** $q=6,318$ cal/g),

m_F : mass of the standard fuel sample (g),

l_{wire} : length of the wire (centimeter),

q_{wire} : heat of combustion per centimeter of the ignition wire (2.3 cal/cm),

ΔT = change of temperature before and after combustion (K).

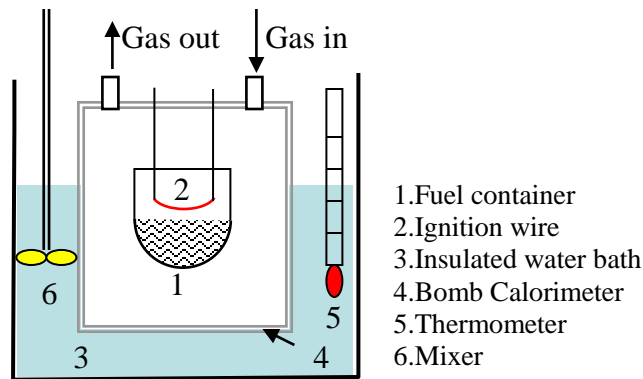


Fig.1 Schematic of bomb calorimeter.

3. Experiment Descriptions

3.1 Experimental procedures

It's a good idea to start with the high purity carbon as your first fuel sample. You will have to decide on the mass of fuel and the pressure of oxygen (Eq.9) to provide for the combustion reaction. Note that complete combustion will require at least enough oxygen to satisfy the stoichiometric reaction, but usually more oxygen is required to actually achieve

complete reaction. Therefore, you need to know how much oxygen is required from the stoichiometric mass ratio of fuel to oxygen. A bottle of charcoal along with many other fuels is located in the cabinet. Measure out about 1 gram using the [top-loading balance](#) provided. The oxygen pressure is measured using a [pressure transducer](#) mounted on the oxygen tank. The readout is located on the bench and is calibrated in atmospheres. Enter the oxygen pressure as well as a file path on the front panel of the LabView program (**Bomb Calorimeter.vi**). After preparing the bomb and turning the mixer on, run the program to collect about 1 min of base line water temperature data, then ignite the fuel. Typical temperature rises are 2 – 3 degrees C over about 10 min. Analyze your raw data in excel plotting temperature vs. time.

3.2 Experiment projects: determining the heat of combustion

Choose different fuels (**at one solid and two liquid fuels**) in the lab and follow the experimental procedure described above. The heat of combustion (gross heat of combustion) can be computed from the measured temperature change, effective heat capacity, and burned length of the fuse wire by rewriting the above equation as

$$q = \frac{\Delta T * C - l_{wire} * q_{wire}}{m_F} . \quad 11$$

Compare your results with those published in standard reference works.

4. Errors and Assumptions

4.1 Incomplete combustion:

Not all of the fuel becomes CO₂ and condensed H₂O in the final products. For example, some of fuel may be partially oxidized into CO or form soot. As a result, the heat of combustion will be lower than the ideal case. In addition, pressure will affect the final products via the changes of the collision rate between molecules and the chemical equilibrium.

4.2 Impurity of fuel:

Fuel may be contaminated by other substances. For example, when coal containing sulfur is burned not all the sulfur is oxidized as SO₂ but instead carried further to SO₃ which combines with water vapor to form H₂SO₄. Some of the nitrogen in the bomb atmosphere is also oxidized and combined with water to form HNO₃. A correction of 13.8Kcal/mol for HNO₃ and 1.4Kcal/mol for each gram of sulfur converted to H₂SO₄ is generally applied. We will ignore the energy released from the heat of formation of these two side reactions.

4.3 Fuse-wire correction

The fuse-wire generates heat through ohmic losses it presents in the firing circuit and by the heat of combustion of the portion of wire burned. The heat input from the firing circuit will be the same as when standardizing the calorimeter so this requires no correction. However, it would be found that the amount of wire consumed from test to test varies. This is a simple correction and therefore must be included in your determination of the calorific value of fuels. A correction of 2.3 cal /cm should be subtracted from your measurement.

4.4 Adiabatic assumption

The bomb is surrounded by a quasi-adiabatic enclosure. Therefore, a more accurate measurement is obtained by considering the preperiod and postperiod portions of the temperature

vs. time curve. By measuring temperature changes as a function of time before and after the rise period an estimation of the heat transfer through the enclosure can be obtained. The resultant “t” is referred to as the net corrected temperature rise. We will assume no heat is lost or gained by the calorimeter.

4.5 Oxygen

Use the compressibility factor (Z) to determine the validity of the ideal gas law when calculating the molar amount of oxygen in the bomb at high pressures.

4.6 Water condensation

If a part of the water formed from combustion is not condensed, how will the heat of combustion change?

5. Lab report content requirement

- 5.1. Report results and calculations with at least one solid fuel and two liquid fuels.
- 5.2. Compare your data with the CRC published data and calculate the accuracy.
- 5.3. Do the following Error estimations or analysis
 - a. Equipment errors
 - b. Incomplete combustion
 - c. Water vapor or condensation in bomb calorimeter.
 - d. Other possible errors in experiment assumptions.

6. Warnings

- (1) Care must be taken to stay within the design limits of the apparatus. NOT MORE THAN ONE GRAM OF CARBON (7,824 cal or 393.5 kJ/mole) EQUIVALENT of a combustible material may be burned in the oxygen atmosphere of the bomb.
- (2) The oxygen pressure is RESTRICTED TO LESS THAN 2.0 MPa (20 atm).